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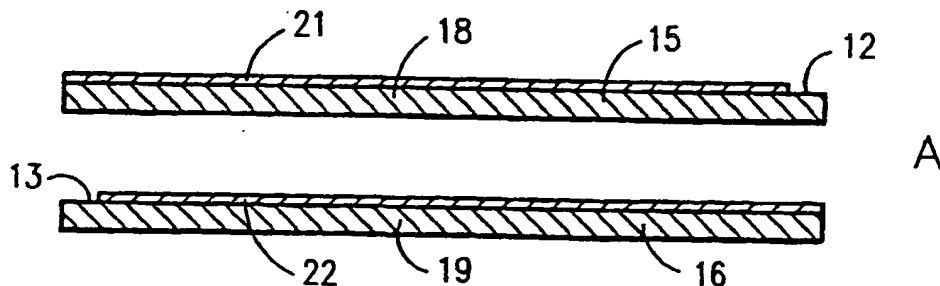
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(54) Title: **LOW COST POLYVINYLIDENE FLUORIDE COPOLYMERS AND METHODS OF MANUFACTURE THEREOF**



(57) Abstract: A material comprises polyvinylidene fluoride (PVDF) in combination with at least one other polymer that is compatible with it. The ratios of amounts of polymer(s) to amounts of PVDF are selected to enhance the properties of PVDF and to lower costs while, in many cases, still improving the properties of the material over PVDF alone. The figure shows a longitudinal sectional view of a capacitor that uses the material of the invention. Film layers (15, 16) are shown with unmetallized margins (12, 13), dielectrics (18, 19), unmetallized portion (21) and metallized portion (22).

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LOW COST POLYVINYLIDENE FLUORIDE COPOLYMERS AND METHODS OF MANUFACTURE THEREOF

Cross-Reference to Related Applications

5 This application is a continuation-in-part of co-pending U.S. patent application Serial No. 09/337,224, filed June 22, 1999, of the same inventor and assignee.

Background of the Invention

10 The present invention relates generally to polyvinylidene fluoride (PVDF) copolymers, and more particularly to structures and methods of manufacture of PVDF copolymers that can be produced at significantly low cost with increased dielectric constant, and dielectric strength, improved chemical and physical resistant properties, and low dissipation factor compared to the prior art homopolymer polyvinylidene fluoride.

15 Polyvinylidene fluoride is the homopolymer of 1,1-difluoroethene and is used in many applications including semiconductor device processing, pulp and paper processing, nuclear waste processing, capacitors, batteries, sensors, food and pharmaceutical processing, and general chemical processing. Its advantages include high purity, chemical resistance to halogens and hot acids, resistance to radiation, high temperature applications (up to 125° C (degrees Celsius)), increased impact strength at ambient and colder temperatures and increased clarity. However, the material is difficult to process into ultra-thin films and in some solid applications and is very costly.

20 The polar polymer PVDF exhibits a large dielectric constant (~12) and demonstrates excellent piezoelectric and pyroelectric properties. PVDF is a partially crystalline linear polymer with a carbon backbone in which each monomer {CH₂-CF₂-} unit has two dipole moments, one associated with CF₂ and the other with CH₂. In the crystalline phase, PVDF exhibits a variety of molecular conformations and crystal structures depending on the method of preparation. The extruded or cast material usually contains 40 and 60% crystalline material in one or both of the principal crystalline phases, alpha and beta. The alpha phase predominates in material cast from the melt. This phase is converted to the beta phase by mechanical deformation of the material at temperatures less than 100° C. In commercial production for film capacitors and sensors, PVDF film
30 is extruded and mechanically stretched both parallel and perpendicular to the direction of

extrusion, as are most of the capacitor grade film dielectrics. This causes a preferred orientation of the polymer chains in the plane of the film and also converts a large percentage of crystallites to beta form.

It is this bi-axially oriented film material which, after polarization, forms the basis of piezoelectric and pyroelectric devices. Unfortunately, the highly crystalline structure also results in some weakness in the physical strength of the film. This causes major problems during the manufacture of very thin films in gauges of less than 5 microns (μm). The material tears quite readily in the machine direction. Another problem that is inherent with this material as a result of its highly crystallinity is poor metal-to-polymer adhesion typically seen in prior art films. In addition, because of its highly crystalline form, solid PVDF structures are quite hard and brittle despite the fact that the material is strong and chemical resistance. For example, tubings produced from this material are not as flexible as tubings made from polyethylene (PE) or polypropylene (PP). Such PVDF structures can cause aging problems when in use and result in poor integrity.

Metallized film capacitors offer the highest volumetric and gravimetric energy densities and reliability of all designs of film capacitors and offer higher pulse power capabilities than foil and other designs. Early film capacitors for high pulse power applications were of dielectric film/foil construction, impregnated with dielectric fluid that filled any voids between layers, and typically had energy densities of less than one joule per cubic centimeter (J/cc). More recent improvements to these pulse power devices include use of metallized polymer films as the dielectric, providing higher energy density and greater reliability. Fluid impregnated film capacitors have a very narrow operating temperature range while the metallized version can operate up to 100° C with the exception of polyphenylene-sulfide (PPS) and polytetrafluoroethylene (PTFE), which can reach an operating temperature of 200° C. Plastic film capacitors can be tailored for very high voltages simply by adjusting the film or dielectric thickness in the capacitor.

The thin metallization layer on a metallized film capacitor is capable of vaporizing away if a short circuit or a weak location occurs somewhere in the dielectric. This phenomenon is known as self-healing or clearing. Clearing should only result in metal oxide insulator formation. Weak locations are usually caused by localized thin spots, or "bubbles," during film manufacture, or due to an impurity within or on the surface of the film, or due to a conductive "track" within the dielectric layer. These are adverse features

that are common to all polymer film dielectric materials.

For high pulse power applications, metallized film capacitor dielectrics typically have been either PP or PVDF, the former being the preferred polymer for high repetition rate applications because of its extremely low dissipation factor (DF), while the latter is the preferred polymer for low repetition rate applications because of its high dielectric constant (12) compared to films such as PP (2.5). To the knowledge of the applicant herein, the highest energy density attained to date using PVDF film material in high pulse power devices is about 2.4 J/cc. PVDF appeared to have promise in various applications, but suffers from non-linearity of capacitance with voltage, very poor insulation resistance, poor clearing ability, high leakage current, relatively low voltage breakdown, poor mechanical properties, and unavailability in thin gauge and uniform thickness. PVDF suffers from poorer performance at elevated temperatures, with application of voltage producing a larger number of clearing sites than at room temperature. In addition, PVDF has relatively high cost. While PP has a poor dielectric constant that limits its overall energy density, it is otherwise an excellent dielectric insulator.

PVDF material used in lithium ion polymer electrolyte batteries as the electrolyte undergoes significant swelling by as much as 15-20% when in contact with liquid organic solvents and at elevated temperatures in excess of 60° C the material begins to dissolve. This causes loss of mechanical integrity of the electrolyte and separator property that could lead to an electrical short. PVDF film used in high energy density film capacitors offers the highest energy density of any dielectric material but is a very unstable material and suffers from high dissipation factors and lower breakdown voltages. PVDF film used in piezoelectric sensor also suffers from the same problem of instability and inconsistency performance.

Despite these problems, PVDF does offer unique properties required for a particular application that may not be available from another material. However, a further drawback to the use of PVDF for many applications is its very high cost. In many cases, the cost of this raw material is as much as fifteen to twenty five times that of another polymer material that may only lack one or two qualities of PVDF. For example, polyester film material for film capacitor application currently costs approximately \$0.50 per pound, while PVDF film may cost as much as \$10.00 per pound. Although these comparative costs are based on economies of scale, the precursor material used to make

PVDF is extremely costly compared to the precursor material used to make other polymers. It is likely that if the properties of this material can be improved together with sufficient reduction in its cost and improvements in its production process, the material would find greater use and would compete effectively in the marketplace with the more common commodity materials such as polyester, polypropylene, etc.

It is a principal objective of the present invention to overcome many of the problems of PVDF polymer used in a variety of different forms for different applications and offer an alternative with significantly improved performance capabilities over these prior art devices.

In a novel capacitor design of the applicant herein described in co-pending U.S. patent application Serial No. 09/065,131, the film capacitor utilizes a wound bi-layer of PVDF and PP (i.e., four film layers in total are wound together in that instance, instead of the traditional method of winding two single layers of similar polymer films with a metallization layer between the two dielectrics) that combines the excellent insulator properties of PP with the excellent dielectric constant of PVDF, to obtain a performance improvement of more than 50% over a single PVDF layer. The improvement is enhanced by increasing the breakdown strength of PVDF/PP combined material when compared to PVDF alone. Nevertheless, variations in thickness and film quality of the bi-layers, intrusion of air between the bi-layers during winding (ϵ for air is 1, with breakdown voltage of only 3 volts per micron compared to several hundred volts per micron for either PVDF or PP and significantly higher dielectric constant), differing thermal electrical properties of the PP and PVDF films in the bi-layers, physical adhesion compatibility issues of the bi-layers, as well as the instability of PVDF homopolymer film, and lack of optimum insulation properties, may combine to limit the long-term reliability of the prior design. By winding four layers together, a greater probability exists of introducing poor uneven windings as a result of the variation in the film thickness. In addition, the prior design does not alter the chemical or electrical properties of the homopolymers, i.e., PVDF is still PVDF, with poor individual electrical properties, and PP is still PP, with poor dielectric constant. In addition, the polar form of PVDF still remains as long as it is in a homopolymer form and just a physical lamination of PVDF and PP.

In co-pending U.S. patent application Serial No. 09/337,224, filed June 22, 1999 (the "224 application"), of which the present application is a continuation-in-part, the

applicant herein has disclosed a much improved novel capacitor design which overcomes many of the problems of the prior art, and of the aforementioned prior design, through the use of two single layers of new designs of hybrid copolymer film materials in the construction of metallized film capacitors similar to the construction of traditional film capacitors. The invention reduces the introduction of air intrusion during capacitor construction, as observed in the construction of four film layers, since only two film layers are used -- hence, increasing the probability of obtaining high performance of the improved film material rather than manufacturing flaws. It also provides a more precise method of tailoring polymer blends with specific film properties for specific applications that cannot be achieved from homopolymer film whether the latter are single layer or combined as bi-layer, tri-layer, etc., films. Since the new material is a copolymer solid solution as opposed to a homopolymer bi-layer, the two copolymer layers used in capacitor fabrication do not present the same thermal/electrical issues as are described above for PVDF/PP bi-layer winding.

A number of new designs of film material are possible with the invention disclosed in the '224 application simply by choosing the appropriate initial materials and tailoring the blends for the intended application. For example, in the design and construction of a capacitor for an implantable defibrillator that would require about 5 or more Joules per cc, the selection of a material with a very high dielectric constant, good clearing ability and breakdown voltages would be necessary and desirable. A representative example of two polymers that could be blended into a copolymer to meet these needs is PVDF and PP, but the composition chosen and the specific percentages of the components will depend on the specific requirements of the film capacitor in each particular instance. In this example, by blending the two resins and manufacturing thin films of the copolymer, a material can be obtained in which the highly polar activity of PVDF is reduced and stabilized through the formation of the copolymer. The reduction in the polarization activity is further reflected in the improvements in the electrical properties of the film, including an increase in the breakdown voltage and insulation resistance of the copolymer compared to PVDF alone, and the ability to be manufactured in thin film with increased physical strength through the reduction in the crystallinity of the copolymer. The result is a material with enhanced energy density and electrical stability over PVDF homopolymer alone.

Such design principles are readily extended to other polymeric insulators such as

polyester, or polycarbonate or any other dielectrics to tailor special properties desired for a particular application. Very thin metallized film capacitors designed in accordance with this hybrid copolymer technique -- which is not limited to a blend of only two polymers but may extend to three or more -- enable achieving a device with stable dielectric constant and, hence, stable capacitance with voltage, improved insulation resistance and clearing or self-healing ability, lower leakage currents, and higher voltage breakdowns (compared, for example, with homopolymer PVDF), with the potential for unprecedented energy density from a bulk capacitor system. The markedly higher performance values (energy density, reliability, weight) is anticipated to be matched by markedly lower cost per unit of performance when volume manufacturing is employed.

Another example of the use of these techniques to achieve new designs is in the development of capacitors for high temperature applications. For example, PPS and PTFE have operating temperature ranges up to about 200° C. Although PTFE can be used at slightly higher temperature, at higher temperatures the electrical properties of the dielectric become very poor. By combining blends of PVDF and PP with either PPS or PTFE in different proportions, the energy density of the capacitor can be increased, and the breakdown strength and other electrical properties can be stabilized for use of the material at temperatures in excess of the indicated range of the homopolymer. This can also be applied to moderate temperature range polymer films such as polyester (PET), polyethylene-naphthlate (PEN) or polycarbonate (PC), to enhance the electrical properties simply by stabilizing with one or more hybrid copolymer components consisting of at least one non-polar group.

Another objective of the present invention is to provide improvements, enhancements and expansions in applications of polymeric blends, particularly in film form but conceivably in other forms as well, of the principles of the invention disclosed in the '224 application.

Summary of the Invention

The primary object of the present invention is to provide a polymer material with the following properties, namely, improved dielectric constant, improved breakdown voltage, improved dissipation factor, improved clearability, lower leakage (and hence higher insulation resistance), higher operating temperature capabilities, higher impact

strength, greater flexibility, reduced brittleness, greater tear-resistance properties (in films), easier processing of both solids and films, easier processing of ultra-thin films of less than 5 μm , greater adhesion of metal-to-polymer in metallized polymer films, reduced resistance to cracks, lower crystallinity, improved aging characteristics, reduced swelling characteristics when in contact with liquid solvents greater dimensional stability, consistent electrical performance, and above all, lower cost. This is achieved by providing a hybrid polymeric material which is a unique copolymer solid-solution blend of PVDF material and at least one polymeric material component with improved stable dielectric, higher temperature resistance or improved mechanical properties. The invention is not limited to two types of polymer blends but can be extended to three or more resin blends to tailor the appropriate properties.

By way of example and not of limitation, for capacitor applications the applicant herein has found that it is desirable to use another polymeric material in combination with PVDF that is preferably another dielectric material with high dielectric constant and one that is less crystalline than PVDF or preferably amorphous. In an extension of the invention disclosed in the '224 application, and in accordance with the present invention, a non-traditional capacitor film material is incorporated or blended with PVDF material for film capacitors in a concentration of 1 to 99% by weight of either material, with the balance being the other material, to provide a hybrid copolymer material with excellent electrical properties as described above. The non-traditional capacitor film material to be blended with PVDF may, for example, be polyacrylonitrile (PAN), polyvinyl chloride (PVC), oligomer of polyvinyl acetate (PVAC), polymethylmethacrylate (PMMA), polyethylene oxide (PEO), acrylic-based polymers, polytetrafluoroethylene-co-hexafluoropropylene (FEP), or polytetrafluoroethylene-co-perfluoro(alkylvinyl ether) (PFA). All of these materials are amorphous to a large extent and their incorporation into PVDF increases the flexural properties and mechanical strength of the film, allowing it to be stretched into a very thin film. In addition, these materials allow greater metal-to-polymer adhesion than the homopolymer PVDF. By forming these blends for film capacitors, the cost of the final copolymer is markedly reduced.

According to one preferred embodiment and method of the present invention, homopolymers of high purity (i.e., greater than 99%, preferably greater than 99.9%, pure) PVDF and PAN resins are blended and co-extruded (e.g., by twin screw blending) with

homogenization to form a melt-cast hybrid copolymer dielectric film. The process results in a thick film, e.g., having a thickness at the lower (thinner) end of a range from about 100 to 200 microns, which requires stretching to make it thinner. The concentration of PVDF in the polymeric hybrid is 1 hundredth to 99 hundredths parts by weight of PVDF, with the balance PAN (i.e., 99 hundredths to 1 hundredth part PAN).

It will be understood, however, that a specific constituent or concentration of either (or any) constituent in a polymeric blend according to the invention is adjusted so as to tailor the properties of polymeric dielectrics for different applications. For an implantable defibrillator, for example, high energy density is required as well as good DF and breakdown voltages. It is noteworthy that in the invention of the '224 application, the PVDF content is maximized for such energy requirement and balanced accordingly with PP to stabilize the poor electrical properties of PVDF. PAN has a dielectric constant of about 6.5 and PVAC has a dielectric constant of about 8.3, and in such instances of dielectric constant the concentration of either of these polymers may be increased in the blend so as to reduce the cost of the copolymer, provided the electrical or other properties desired for the final film can be achieved. However, to obtain some desired property(ies) other than simply energy density, it may be necessary to reduce the concentration of PVDF to as low as 1 part PVDF to 99 parts PAN. An optimum composition for high performance may be in the ratio of at least 1:1, but the specific ratio or concentration of the various component resins in the blend do not constitute a limitation on the breadth or scope of the present invention.

The hybrid copolymer film material of the invention offers high dielectric constant, improved stability, improved dissipation factor, improved clearing ability, and high breakdown voltage. Although this film is particularly well suited for film capacitor applications, it is also useful in electrical cables, magnetic tapes, optical films for security and other purposes, piezoelectric sensors, and food packaging, to name a few other applications.

Although a two-polymer blend represents a preferred embodiment, with at least one non-polar component in the blend, the present invention is readily extended to a three or more polymer blend which tailors the specific properties desired for the final polymer. The preceding brief description of copolymer blends comprising PVDF and PAN is provided merely for the sake of simplicity and clarity of exemplary embodiments of the

invention for high energy density capacitors for use in implantable defibrillator and other high pulse power applications. It will be understood by those skilled in the art that other polymer hybrid blends may be fabricated from a combination of two or more of PVDF, PP, PEN, PPS, PC, PET, PTFE, PAN, PVA, PPO, PAN, PVC, PVAC, PMMA, FEP, PFA or other polymeric materials possessing high insulation resistance properties. For example, design and fabrication of a hybrid copolymer blend film material for improved or higher temperature applications and with improved electrical properties, may be achieved using a tertiary copolymer blend of PPS, PVDF and PP.

The hybrid copolymer of the invention enables the design of very thin metallized film capacitors with stable dielectric constant and stable capacitance with voltage, as well as improved insulation resistance and clearing or self-healing ability, lower leakage currents and higher voltage breakdown compared, for example, with homopolymer PVDF, with the potential for energy density greater than 8 J/cc from a bulk capacitor system. This represents a more than three-fold increase over state of the art PVDF film capacitors, and a more than six-fold increase over other polymer films, in energy density. Moreover, the cost of the hybrid copolymer of the present invention, and of film capacitors using the same, is anticipated to be about 50% of the present-day cost of homopolymer PVDF and existing film capacitors on a per unit energy basis, with the economies of scale of volume manufacturing.

Yet another objective of the present invention, then, is to provide such hybrid film materials constituting blends of PVDF with one or more polymers from among PP, PEN, PET, PPS, PTFE, PC, PPO, PAN, PVC, PVAC, PMMA, FEP, and PFA, for example, and various copolymers of such materials. Preferred manufacturing methods for the production of such hybrid copolymer films include, for example, bi-axial extrusion, blown bubble process, melt cast or solvent casting techniques, and vapor deposition onto a substrate.

Another objective of this invention is to provide electrically stable copolymer materials of PVDF that still maintain very high activity in piezoelectric sensors. The applicant has found that the incorporation of fluorinated compounds such as polytetrafluoroethylene-co-ethylene (E/TFE), polychlorotrifluoroethylene (PCTFE), polychlorotrifluoroethylene-co-ethylene (E/CTFE), polyvinyl fluoride (PVF), PTFE, FEP or PFA into PVDF (i.e., in blends) in a wide range of compositions provides a copolymer

material with enhanced stability and improved consistency in the piezoelectric activity of the copolymer over that obtained from the homopolymer PVDF. The fluorine molecules from the second polymer appear to radically alter the dipoles of the C-H and C-F bonds and result in a material that is less erratic with applied voltage. Although fluorinated compounds appear to provide the best performance improvement, they are relatively more expensive than the common dielectric materials and, hence, do not furnish as great a cost reduction in the final hybrid copolymer PVDF film product as the latter materials. Materials based on non-fluorinated dielectric film capacitor materials such as PP, PEN, PET, PPS, PC, PPO, PAN, PVC, PVAC, and PMMA, also provide excellent piezoelectric activity and are significantly less expensive due to their voluminous use in numerous commodity applications. Particularly desired materials for use with PVDF in piezoelectric sensors are either PP or PET, which are very readily available and whose cost is about 15 to 20 times less than the fluorinated materials.

Another objective of this invention is to provide PVDF copolymer materials that can be produced at low cost and yet provide the same performance requirements of PVDF for a wide range of applications, including characteristics such as higher temperature resistance, increased chemical resistance, higher impact strength, lower brittleness, easier processing, flexibility, creep resistance, mechanical shock resistance, toughness, high abrasion resistance, improved aging characteristics, resistance to weathering, resistance to ultra-violet and nuclear radiation, reduced swelling properties when in contact with liquid solvents, and improved thermal conductivity. Through the development of various copolymer blends of PVDF and other compounds in enhancing the electrical properties of high energy density film capacitors, the applicant herein has found that those materials described in the '224 application as well as some other new material copolymer blends serve to enhance or provide equivalent physical and chemical properties to those of PVDF, at considerably lower cost. These materials include, PP, PEN, PET, PPS, PTFE, PC, PPO, PAN, PVC, PVAC, PMMA, FEP, PFA, E/TFE, PCTFE, E/CTFE, and PVF.

Higher temperature resistance capabilities can be obtained by incorporating PVDF with either PP, PPS, PTFE, PPO, PAN, E/TFE, PCTFE, E/CTFE, PFA and FEP. Most of these materials from the second polymer group are temperature resistant up to 250 °C while PVDF is temperature stable up to 175 °C. Blending a higher temperature material with PVDF results in material with improved heat resistance properties over PVDF.

Increased chemical resistance, improved aging characteristics, and resistance to weathering are best obtained by incorporating PVDF with either PP, PTFE, PPO, E/TFE, PCTFE, E/CTFE, PFA, FEP, and PET.

Higher impact strength, lower brittleness, creep resistance, mechanical shock resistance and toughness, radiation resistance, lower swelling, improved thermal conductivity and high abrasion resistance, are best obtained by incorporating PVDF with thermoplastic polymers such as PP, PTFE, FEP, PFA and PET. Swelling as low as 5% has been observed when PVDF is combined with these materials, and the copolymers are stable up to 100 °C in liquid organic solvents such as diethyl carbonate and propylene carbonate.

Increased flexibility, easier processing of the material in any form, and tear resistance of thin film materials, are best obtained when PVDF is combined with PP, PET, PEN, PPS, PAN, PVA, PVAC, PMMA, and PVC. These materials in the second group provide plasticizing properties and flexible backbone to PVDF and allow easier processing of the copolymer into thin films or solid form, and offer improved tear resistance in both the machine direction and transverse direction. Further, they are available in a wide range of molecular weights, allowing use of an appropriate molecular weight second polymer depending upon the desired characteristics for the final polymer.

The concentration of PVDF in the polymeric hybrid for the various physical features is 1 hundredth to 99 hundredths parts of PVDF, with the balance being the second polymer (i.e. 99 hundredths to 1 hundredth part of second polymer). It will be understood, however, that a specific constituent or concentration of either (or any) constituent in a polymeric blend according to the invention is adjusted so as to tailor the properties of the final polymer for different applications. The optimum composition should be chosen that delivers the desired properties of PVDF and yet is incorporated in such a concentration with the second polymer so as to result in significantly lower cost. As mentioned earlier herein, fluorinated ones of the second group polymers are not as attractive from a cost standpoint.

Although a two-polymer blend including PVDF represents a preferred constituency, the present invention is readily extended to a three or more polymer blend in which the other polymer(s) is selected to tailor the specific properties or characteristics desired for the final copolymer.

Brief Description of the Drawings

The above and still further aims, objectives, features, aspects and attendant advantages of the present invention will become apparent from the following detailed description of certain preferred embodiments and methods of fabrication of hybrid copolymers and copolymer films in accordance with the invention, constituting the best mode presently contemplated of practicing the invention, when taken in conjunction with the accompanying drawings, in which:

FIG. 1 is a perspective view of a wound metallized film capacitor, which utilizes a hybrid copolymer PVDF film according to the present invention;

FIG. 2A and **2B** are, respectively, a longitudinal sectional view and a cross-sectional view, and **FIG. 2C** is a side view, of the film capacitor of **FIG. 1**; and

FIG. 3 is a flow chart of an exemplary method of manufacturing the capacitor of **FIG. 1**, which includes a method of producing .

Detailed Description of Presently Preferred Embodiments And Methods

In an exemplary film capacitor application, homopolymer PVDF is used in combination with another polymeric material to provide a hybrid copolymer for the dielectric film. Preferably the other polymeric material is another dielectric with high dielectric constant and which is preferably amorphous, but at least less crystalline than PVDF. In one preferred embodiment of the film material, a non-traditional capacitor film material is the other material incorporated or blended with PVDF material in a concentration of 1 to 99% by weight of either material, with the balance being the other material, in a specific ratio tailored to provide desired physical or electrical properties of the end product. For example, the other polymer material may be PAN, PVC, oligomer of PVAC, PMMA, PEO, an acrylic-based polymer, FEP, or PFA, all of which are substantially amorphous. Incorporating any one or more of such material into PVDF increases the flexural properties and mechanical strength of the resultant hybrid copolymer film, so that it may be stretched into a very thin film.

PVDF resin and another or other homopolymer resins of purity greater than 99% (preferably greater than 99.9% pure), such as PAN resin, are blended within the one of the aforementioned concentrations or ratios and co-extruded such as by twin-screw blending.

With its dielectric constant of about 6.5, PAN's concentration in the blend may be increased as necessary to provided desired electrical or other properties of the hybrid copolymer film, and with that increased concentration a reduction in cost of the resulting film is achieved. The blend is homogenized to form a melt-cast hybrid copolymer, thick dielectric film. Its thickness may be at the thinner end of a range from about 100 to 200 microns, and the film may be subsequently stretched without tearing, to make it thinner.

As emphasized earlier herein, although such films are quite suited for film capacitor applications, the principles of the present invention may be used to produce the same or similar films in other constituencies and ratios of blended polymer materials, one of which is PVDF, which in that way are tailored for other applications such as in electrical cables, magnetic tapes, optical films for security and other purposes, piezoelectric sensors, and food packaging, to name a few.

Rather than a two-polymer blend, which is a preferred embodiment, with the polar constituent PVDF and a non-polar constituent, a three or more polymer blend also incorporating PVDF may be used, with the plural constituents and their ratios selected to tailor the physical properties of the resulting hybrid copolymer film to a particular application. Such films may be fabricated from a combination with PVDF of one or more of PP, PEN, PPS, PC, PET, PTFE, PAN, PVA, PPO, PAN, PVC, PVAC, PMMA, FEP, PFA or other polymeric materials possessing specifically desired physical property or properties. By way of example, a tertiary copolymer blend of PPS, PVDF and PP may be formed to produce a hybrid copolymer blend film with improved electrical properties and adapted for high temperature applications. Whether two-, three- or more polymer blends, these hybrid copolymer films may be manufactured by use of any of a number of different processes, including bi-axial extrusion, blown bubble process, melt cast or solvent casting techniques, and vapor deposition onto a substrate.

Electrically stable copolymer materials of PVDF which are highly suitable in piezoelectric sensor applications include PVDF into which is incorporated fluorinated compounds such as E/TFE, PCTFE, E/CTFE, PVF, PTFE, FEP and/or PFA in a wide range of compositions. Such copolymer materials possess enhanced stability and improved consistency in piezoelectric activity. Although the specific mechanism is not known to applicant, it is hypothesized that the fluorine molecules from the additional polymer (to PVDF) radically alter the dipoles of the C-H and C-F bonds and offer greater

stability of the resultant film with applied voltage. The major drawback to the use of fluorinated compounds in the copolymer is their cost, which lessens the extent of cost reduction of the copolymer blend over homopolymer PVDF. Non-fluorinated, readily available polymeric materials include PP, PEN, PET, PPS, PC, PPO, PAN, PVC, PVAC, and PMMA, which possess desirable properties and offer a significant cost advantage over the fluorinated compounds. PP or PET blended with PVDF are especially desirable in piezoelectric sensor applications.

Hybrid copolymer films including PVDF with one or more other polymers of selected properties and participation according to the invention enable production of very thin metallized film capacitors of stable dielectric constant and capacitance, improved insulation resistance and clearing ability, lower leakage currents and higher voltage breakdown compared with homopolymer PVDF, and offer energy density greater than 8 J/cc.

A hybrid copolymer film according to one exemplary embodiment of the invention, used in a capacitor shown in FIGS. 1, 2A, 2B and 2C, is prepared as a part of the manufacturing process illustrated by the flow chart of FIG. 3. The process commences with the mixing of homopolymer PVDF with one or more homopolymer components from polar or non-polar groups. Where the capacitor application is a high energy film capacitor for an implantable defibrillator, for example, PP is quite suitable as the latter homopolymer component in combination with the PVDF. The homopolymer high purity PVDF (Solvay) and PP (Exxon) resins are fed separately into a co-extruder (twin screw) via hoppers, where the resins are blended with homogenization to form a resin melt-cast dielectric film. Alternatively, the blending may be performed by a process known as compounding, wherein the two resins are fed into an extruder in the desired ratio, melted together and extruded in a new resin blended pellet which is a composition of the constituents PVDF and PP. These methods of blending perform equally well to produce a finished film with characteristics or properties adapted to increase metal-to-polymer adhesion.

Any concentration of PVDF to PP (PVDF:PP) in the hybrid copolymer film in a range consisting of from 1 to 99 parts of PVDF by weight with the balance PP (i.e., from 99 parts to 1 part of PP) may be suitable for purposes of a particular application of the film, although the specific ratio will be adjusted to tailor the film properties to the specific

application. As a principal objective of the present invention is to take advantage of desirable properties of homopolymer PVDF in various applications, while reducing its contribution of comparatively high cost in the final product, it will be desirable to incorporate a relatively large percentage of the lower cost polymer(s), such as PP, in the hybrid copolymer form, provided that does not result in significant adverse properties or characteristics for the specific application in which the copolymer is used.

Biaxial orientation of the final film is preferred, such orientation referring to orientation of the crystalline structure of the film, and adaptability of the film to stretching in two directions, namely, the machine direction and the transverse direction. The most common processes for biaxially orienting films are (i) the flat die tentering frame process and (ii) the double-bubble (blown) process. An extruded method is preferred over the so-called "blown bubble" process, to achieve closer thickness tolerances.

In the flat die tentering frame process the polymer blend is fed into a flat die with one or more extruders. The resulting molten plastic sheet is solidified by extrusion onto a chilled drum, and the solidified sheet is then stretched in machine direction orientation (MDO, i.e., in the direction of the film travel) by a series of rollers moving at a higher line speed than the chilled drum. Operating conditions of the extrusion process, including temperature, throughput, die opening and width, etc., may be adjusted until a good quality melt-cast film is obtained. The operating conditions will vary for each composition even if the resin materials are the same. For multi-resin extrusion, the resin pellets are mixed according to the type of extrusion system available. For example, for a tertiary component system, resin copolymers of PVDF and PP might be formed as one component and either PPS or PC or PET or PEN used as the second component in a twin screw extruder. Alternatively, the entire resin pellets of the mixture may be melted before extrusion into a melt-cast.

Even though PVDF melts at 171° C and PP melts at 189° C, the resin melt is usually at significantly higher temperatures, typically at about 250° C to 300° C. Because of the higher temperature of the resin melt, adequate heat exists within the polymer during injection of the melt to allow stretching to a thinner sheet before ultimately being stretched further and pulled wider to a still thinner sheet during MDO.

The extrusion temperature and the throughput of the individual resin vary depending upon the formulation composition, and the throughput die opening and width

depend upon the desired thickness and width of the final film. Typically, these parameters are varied to achieve a melt-cast resin thickness in a range from about 100 to 200 microns, with preference for the thinner end of this range, so as to achieve a final film thickness of about 4 microns at the end of the processing run, and a width in a range from about 20 to 30 inches. Hence, if a final film thickness of about 2 microns is desired, the starting melt-cast thickness should be in a range from about 50 to 100 microns. The wide range of variation is attributable to the stretching and thinning differences of the polymers used. Processing at various stages must be adjusted to obtain the most optimum film desired without breaking, wrinkling, or overheating of the film web, for manufacture at the desired rate. Typically, achievement of a good quality film means that the film is clean and free of dust or specks; has no bubbles, pinholes or other visible inclusions or impurities within the film; is static-free (to preclude attracting dust particles); and is wrinkle-free, to mention its principal attributes.

The melt-cast film is then bi-axially oriented, first being pulled along and through several rollers for feeding it under proper tension into the MDO heated chamber, where it is stretched so as to exit the chamber with a typical film thickness in a range from about 25 to 50 microns. The MDO chamber has a series of rollers and a tension control system by which the film is stretched in the direction of film travel to produce a thinner film with a more uniform thickness. The film exits the MDO chamber at a speed which is faster than that at entry, depending upon the film thickness at the end of the MDO run. For example, a melt-cast film thickness of 100 microns at entry into the MDO chamber, which is stretched therein to a film thickness of 25 microns, will exit the MDO chamber at four times its entry speed. Here again, the process parameters in the MDO chamber are adjusted — to control conditions such as line speed, film tension, stretching ratios, and so forth, for optimum film quality and desired final thickness. These conditions are dependent not simply on the final film thickness, but primarily on the properties of the resin. The parameters chosen in the first stage of the film processing, i.e., extrusion and melt-cast film production, will affect the parameters chosen in the second stage of the film processing, i.e., the MDO stretching.

With continuing reference to the flow chart of FIG. 3, the thinner film exiting the MDO chamber is fed through additional rollers to maintain proper tension, and then enters the transverse direction orientation (TDO) chamber where it is stretched in the transverse

direction by the tenter frame method. This is a conventional technique in which the film is seized by a continuous series of mechanical jaws at both ends of the film width just before it enters the TDO chamber. As with the MDO chamber, the TDO chamber is heated. The latter chamber typically has a length ranging from about 40 to about 100 feet, depending on the extent of film production. Width of films being processed through the chamber may vary from two meters to several meters.

As the film moves forward in the TDO chamber, the mechanical jaws move outward and thereby stretch the film to make it thinner and wider, typically to a final thickness in a range from about 0.5 to 25 microns and a width in a range from about 80 to 400 inches. At the opposite (i.e., exit) end of the TDO chamber, the jaws are automatically actuated to release the further thinned and widened film for winding onto paper or plastic cores. As a result of the stretching, the speed of the film at exit from the TDO chamber is considerably faster than the film speed at entry. For example, a film with 100 micron melt-cast thickness exiting the MDO chamber at 25 microns thick travels at four times the speed at entry, as noted above, and if it has then been stretched to a final thickness of 2.5 microns, will exit from the TDO chamber with a speed which is 40 times the speed of the original melt-cast film.

Here also, the processing parameters of the TDO chamber will depend upon desired film thickness as well on production feasibility. Film speed and stretching ratio in the transverse direction in the TDO chamber will determine the final film thickness. The dwell time selected for the film in the TDO is also important, as it controls the reduction in film thickness without breakage. Before winding onto paper or plastic cores, the film is trimmed at its edges with blades placed at either end of the film web to avoid film puckering that would otherwise cause wrinkles and other abnormalities in the film, depending upon the application in which the film is to be used, such as to avoid an adverse effect on performance in film capacitor applications. Typically, the place(s) where the jaws seize the film are thicker than the bulk film. The film may also be treated by corona discharge, a known electrostatic surface treatment to further improve its reception of and adhesion to a metal covering layer in capacitor and certain other applications. Once the film has been manufactured and wound onto cores, it can be slit into any size desired.

The base hybrid copolymer film so produced can then be processed further, if desired, to improve its electrical or other properties, at the same or another processing

facility. For example, for purposes of film capacitor applications the film may be coated with another dielectric polymer to enhance the base film properties and may also be metallized with a thin metal layer. As further indicated in the flow chart of FIG. 3, a coating of a polymeric material such as an acrylate may be applied to the base film in a single but continuous step to a thickness in a range from about 0.1 to 2.0 microns. Such a coating may be applied either through casting an acrylate solution directly onto the film and curing the acrylate using electron beam or ultraviolet radiation, or depositing the acrylate via a spray or atomization method followed by such curing. The latter technique is preferred because it allows better control over the thickness of the acrylate layer.

For the capacitor application, the coated film may then be metallized — for example, by spraying a metal (typically, aluminum) onto the moving polymer film via vapor deposition in a vacuum chamber, to a thickness in a range from about 50 to about 500 Å. The desired resistivity of the metal on the polymer film is typically in a range from about 0.1 ohm per square to 1000 ohms per square. The higher the resistance, the better the breakdown voltage of the film dielectric. Before the metallization process is performed, the polymer film is appropriately masked to provide unmetallized margins at the edges of the width of the film 11 as illustrated in the longitudinal sectional view of FIG. 2A, where alternate layers of film 15, 16 (when the capacitor is assembled, as described below) are shown as having these unmetallized margins at 12 and 13, respectively, at opposite edges to prevent electrical shorting of the electrodes of the capacitor 10 when the end metallization is ultimately applied as described below.

Once the polymer has been metallized, it is slit further to the width equivalent to the metallized layer plus an unmetallized margin. Although it is not absolutely necessary to coat the copolymer film with an acrylate or other polymer in the processing of the film for film capacitor manufacture, it is necessary to metallize the film to manufacture metallized film capacitors. However, the advantages of hybrid copolymer films described herein are not restricted in capacitor applications to metallized capacitor manufacturing, but may be readily extended to other types of capacitors such as those incorporating discrete foils, and those involving impregnation by a fluid.

Finally, two separate rolls of the metallized film 15, 16 produced by the foregoing exemplary method are placed in a capacitor winder and wound tightly together on a mandrel 14 (which may subsequently be removed) so that the layers are arranged in the

sequence dielectric 18/metallized portion 21/dielectric 19/metallized portion 22, as illustrated in the cross-sectional view of FIG. 2B. This replicates a typical construction of the capacitor 10, i.e., a dielectric with two metallic plates on opposite sides. The two rolls of film are wound with the margins (12, 13, FIG. 2A) on opposite sides.

5 The extent of winding of the capacitor depends on the physical size of the capacitor desired or on the capacitance desired. The thickness of the copolymer film determines the voltage limit of the capacitor. Tight winding of the two rolls aids in removing any entrapped air that might otherwise cause premature breakdown. Individual capacitors will be processed in a clean room environment of at least class 100, incorporating HEPA
10 filters, to reduce the likelihood of contamination of the contact point between the dielectric film layers by foreign particles as well as reducing moisture intake in the dielectric.

 Electric winding better serves to maintain uniform tension on each capacitor. The length and thickness of the film wound (as at 24, FIG. 2C) in a capacitor 10 are carefully measured so as to accurately calculate the energy density and other electrical parameters
15 of the device. The capacitor 10 is taped at the edges thereof and strapped in a tray open on both sides, to prevent unwinding of the film layers and to allow the edges or ends of the cylinder to be sprayed with a conductive element (25, 26, FIGS. 1 and 2C). To that end, both ends of the capacitor 10 are schooped or metal sprayed with a high zinc content solder (harder material) followed by a regular softer "Babbit" end spray solder of 90% tin,
20 10% zinc. The first spray scratches the metallized surface and creates a trough to achieve better contact with the metallization on the dielectric film. The combination of end sprays further aids better contact adhesion with the final termination. Subsequently, aluminum leads 29, 30 (FIG. 2C), are soldered onto each end to form the final termination. One termination is spot welded to the bottom of an aluminum can, while the other termination
25 is parallel welded to the lid. The capacitor is filled with a liquid impregnate (typically, isopropyl phenyl sulfone, not shown) in vacuum filling apparatus, and is then crimp-closed.

 In a variation of the technique, a homopolymer film may be coated with PVDF, or vice versa, for a particular application in which the advantages of PVDF are desired with
30 enjoyment of a lower cost product. The coating may be performed using a melt casting or solvent casting process, or by vapor deposition or by spraying using an atomizer. The vapor deposition or spray system can deposit the polymer coating from a solution, hot-

resin or melted resin. A higher temperature application of the coating ensures a lower viscosity, thereby allowing the atomized particles to be deposited in the nano size range. Polymer(s) incorporated with PVDF in this manner may, for example, include PET, PP, PPS, PTFE, PEN, PC, PEO, PVA, PPO, PAN, PVC, PVAC, PMMA, FEP, PFA, fluorinated compounds, or acrylates.

Vapor deposition allows the base film (e.g., the PVDF) to be unwound from one roll and wound onto another, while the second polymer is deposited onto that film in a desired thickness by atomizing such as from a solvent-polymer system or a melt-polymer system. The method is readily extended to a second or a third coating to increase the thickness of the coating, or to laminate a second and subsequent layer of a polymer or polymers, which has a different composition from that of the first layer. The method may further be extended to include polymers which are radiation curable, using either ultraviolet or electron beam radiation. Typical radiation curable polymers include acrylates which are available from various manufacturers, including Radcure, in a wide range of different grades and compositions.

The desirable properties of PVDF hybrid copolymer products of the present invention extend to numerous applications beyond film capacitors for medical device or non-medical applications. These include, for example, usage for electric vehicles, compact energy storage devices for laser applications or other pulsed power applications, electrical cables, magnetic tapes, optical films for security and other purposes, piezoelectric sensors, loudspeakers, touch sensors, ultrasonic ranging and imaging devices, automobile bumper sensors, generation of electrical power using a hydro-piezoelectric process, and other active material applications, as well as numerous electrically benign applications such as a wrap for radiation sensitive materials and for chemical protection, and food packaging, among others. Wide scale commercial use of PVDF and its considerable advantageous properties for many such applications has been severely limited by an unavailability of consistently stable high-activity material, but primarily for economic reasons -- the prohibitively high cost of PVDF material. The present invention provides PVDF hybrid copolymer products that take advantage of the desirable properties of PVDF, and in many instances improved properties introduced or produced by the combined polymer(s) for particular applications, with what can be markedly lower cost compared with homopolymer PVDF. The film materials need not be extremely thin, and

in some instances may be desirable processed as thick films. Also, the film need not be biaxially oriented in all or even many applications, this being a desirable feature for the exemplary film capacitor application.

Moreover, although manufacturing processes have been described or cited herein
5 for the production of film materials for capacitors, radiation protection and coating applications, the combined, e.g., blended, polymers may be extruded or otherwise processed for the fabrication of PVDF hybrid copolymer thick sheets, solid blocks and solid or hollow tubing in various sizes. A conventional injection molding process may also be used for producing solid materials through the injection of molten polymers into a die
10 having the desired shape for virtually any form of the final copolymer product, followed by rapid quenching. Blocks of various polymer blends may alternatively be manufactured and subsequently machined to a desired form. The invention is not limited to any particular concentration or ratio of PVDF in the combined polymeric product, nor to a specific process for producing such product.

15 Thus, although certain exemplary embodiments and methods have been disclosed herein, it will be appreciated by those skilled in the art to which the invention pertains, from a consideration of the foregoing description, that variations and modifications of the disclosed embodiments and methods may be made without departing from the spirit and scope of the present invention. Accordingly, it is intended that the invention shall be
20 limited only by the appended claims and the rules and principles of applicable law.

What is claimed is:

1 1. A hybrid copolymer material, comprising polyvinylidene fluoride (PVDF)
2 combined with at least one other polymer compatible therewith, in a ratio of
3 concentrations by weight of the PVDF and said at least one other polymer selected to
4 provide physical properties of said hybrid copolymer material which are tailored to an
5 application in which said hybrid copolymer material is to be used, including enhancement
6 of intrinsic properties of PVDF, and to substantially lower the cost of said hybrid
7 copolymer material relative to the cost of an equivalent quantity of homopolymer PVDF
8 alone.

1 2. The hybrid copolymer material of claim 1, wherein said PVDF is combined
2 with a plurality of other compatible polymers in a ratio of concentrations thereof selected
3 to tailor physical properties of said hybrid copolymer material to the application in which
4 it is to be used.

1 3. The hybrid copolymer material of claim 1, wherein said at least one other
2 polymer is selected from a group consisting of polypropylene (PP), polyethylene-naphthlate
3 (PEN), polyester (PET), polyphenylene-sulfide (PPS), polytetrafluoroethylene (PTFE),
4 polyethylene (PE), polycarbonate (PC), polypropylene oxide (PPO), polyacrylonitrile
5 (PAN), polyvinyl chloride (PVC), oligomer of polyvinyl acetate (PVAC),
6 polymethylmethacrylate (PMMA), polyethylene oxide (PEO), polytetrafluoroethylene-co-
7 hexafluoropropylene (FEP), polytetrafluoroethylene-co-perfluoro(alkylvinyl ether) (PFA),
8 polytetrafluoroethylene-co-ethylene (E/TFE), polychlorotrifluoroethylene (PCTFE),
9 polychlorotrifluoroethylene-co-ethylene (E/CTFE), polyvinyl fluoride (PVF), and acrylic-
10 based polymers.

1 4. The hybrid copolymer material of claim 1, wherein said PVDF and said at
2 least one other polymer are combined in a ratio of concentrations of 0.99 to 0.01 PVDF
3 with the balance being said at least one other polymer.

1 5. The hybrid copolymer material of claim 1, wherein said PVDF and said at

2 least one other polymer are combined in a blend of resins thereof.

1 6. The hybrid copolymer material of claim 1, wherein said PVDF and said at
2 least one other polymer are combined in layers thereof.

1 7. The hybrid copolymer material of claim 1, wherein said at least one other
2 polymer is amorphous.

1 8. The hybrid copolymer material of claim 5, wherein said hybrid copolymer
2 material is produced by at least one of a twin screw extrusion, biaxial extrusion, blown
3 bubble, melt cast or solvent casting process.

1 9. The hybrid copolymer material of claim 6, wherein said hybrid copolymer
2 material is produced by at least one of a vapor deposition or spray process.

1 10. The hybrid copolymer material of claim 9, wherein said PVDF is a thin
2 film, and said at least one other polymer is deposited onto the PVDF film in a desired
3 thickness by atomization from a solvent-polymer system or a melt-polymer system.

1 11. The hybrid copolymer material of claim 1, wherein said hybrid copolymer
2 material is produced in one of thin film, thick sheet, solid block, and solid or hollow tubing
3 form.

1 12. The hybrid copolymer material of claim 11, wherein said hybrid copolymer
2 material is of biaxially-oriented, thin film form.

1 13. The hybrid copolymer material of claim 11, wherein said hybrid copolymer
2 material is produced in its final form for a predetermined application by machining from
3 a solid block of said hybrid copolymer material.

1 14. A hybrid polymeric material, comprising a copolymer solid-solution blend
2 of PVDF material and at least one additional polymeric material component with

3 characteristics of greater dielectric stability, higher temperature resistance or better
4 mechanical properties than PVDF, and wherein said copolymer solid-solution blend has
5 a lower cost of production than an equal quantity of PVDF material alone.

1 15. The hybrid polymeric material of claim 14, wherein said PVDF material
2 and said at least one additional polymeric material component are in concentrations of 1
3 to 99 parts by weight of one and the balance being the other in said solid-solution blend,
4 wherein said concentrations are selected to tailor said hybrid polymeric material to meet
5 performance requirements of a predetermined application in which said hybrid polymeric
6 material is to be used.

1 16. The hybrid polymeric material of claim 14, wherein said copolymer
2 solid-solution blend includes said PVDF material and plural additional polymeric material
3 components selected to tailor said hybrid polymeric material to meet performance
4 requirements of a predetermined application in which said hybrid polymeric material is
5 to be used.

1 17. The hybrid polymeric material of claim 14, wherein said at least one
2 additional polymeric material component is selected from a group consisting of PP, PEN,
3 PET, PPS, PTFE, PE, PC, PPO, PAN, PVC, PVAC, PMMA, PEO, FEP, PFA, E/TFE,
4 PCTFE, E/CTFE, PVF, and acrylic-based polymers.

1 18. The hybrid polymeric material of claim 14, wherein said at least one
2 additional polymeric material component is amorphous.

1 19. The hybrid polymeric material of claim 14, wherein said hybrid polymeric
2 material is produced by at least one of a twin screw extrusion, biaxial extrusion, blown
3 bubble, melt cast or solvent casting process.

1 20. The hybrid polymeric material of claim 14, wherein said hybrid polymeric
2 material is produced in one of thin film, thick sheet, solid block, and solid or hollow tubing
3 form.

1 21. The hybrid polymeric material of claim 14, wherein said hybrid polymeric
2 material is of biaxially-oriented, thin film form.

1 22. The hybrid polymeric material of claim 14, wherein said hybrid polymeric
2 material is produced in its final form for a predetermined application by machining from
3 a solid block of said hybrid polymeric material.

1 23. A method of manufacturing a hybrid copolymer material, comprising the
2 steps of forming a homogeneous blend of at least two preselected polymeric resins one of
3 which is PVDF and the at least one other of which is selected to enhance the overall
4 physical properties of PVDF in said hybrid copolymer material to meet performance
5 requirements of a predetermined application in which said hybrid polymeric material is
6 to be used; and processing said blend into a solid solution toward a final form of said
7 hybrid copolymer material by at least one of a twin screw extrusion, biaxial extrusion,
8 blown bubble, melt cast or solvent casting process.

1 24. The method of claim 23, wherein said at least one other polymeric resin is
2 selected from a group consisting of PP, PEN, PET, PPS, PTFE, PE, PC, PPO, PAN, PVC,
3 PVAC, PMMA, PEO, FEP, PFA, E/TFE, PCTFE, E/CTFE, PVF, and acrylic-based
4 polymers.

1 25. The method of claim 23, wherein said at least one other polymeric resin has
2 an amorphous structure.

1 26. The method of claim 23, including, in said processing step, forming said
2 hybrid polymeric material into one of a thin film, thick sheet, solid block, or solid or
3 hollow tubing.

1 27. The method of claim 23, wherein said at least two polymeric resins are in
2 concentrations of 1 to 99 parts by weight of one and the balance being the other in said
3 blend.

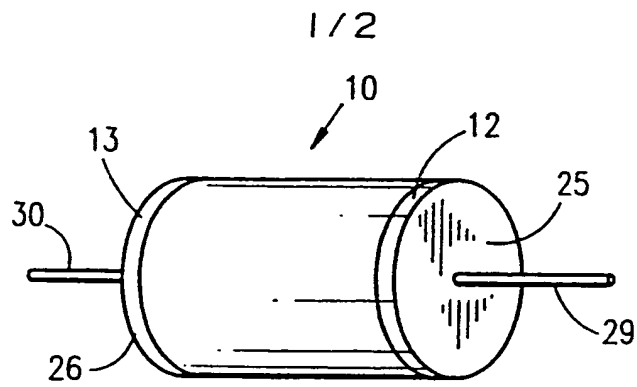
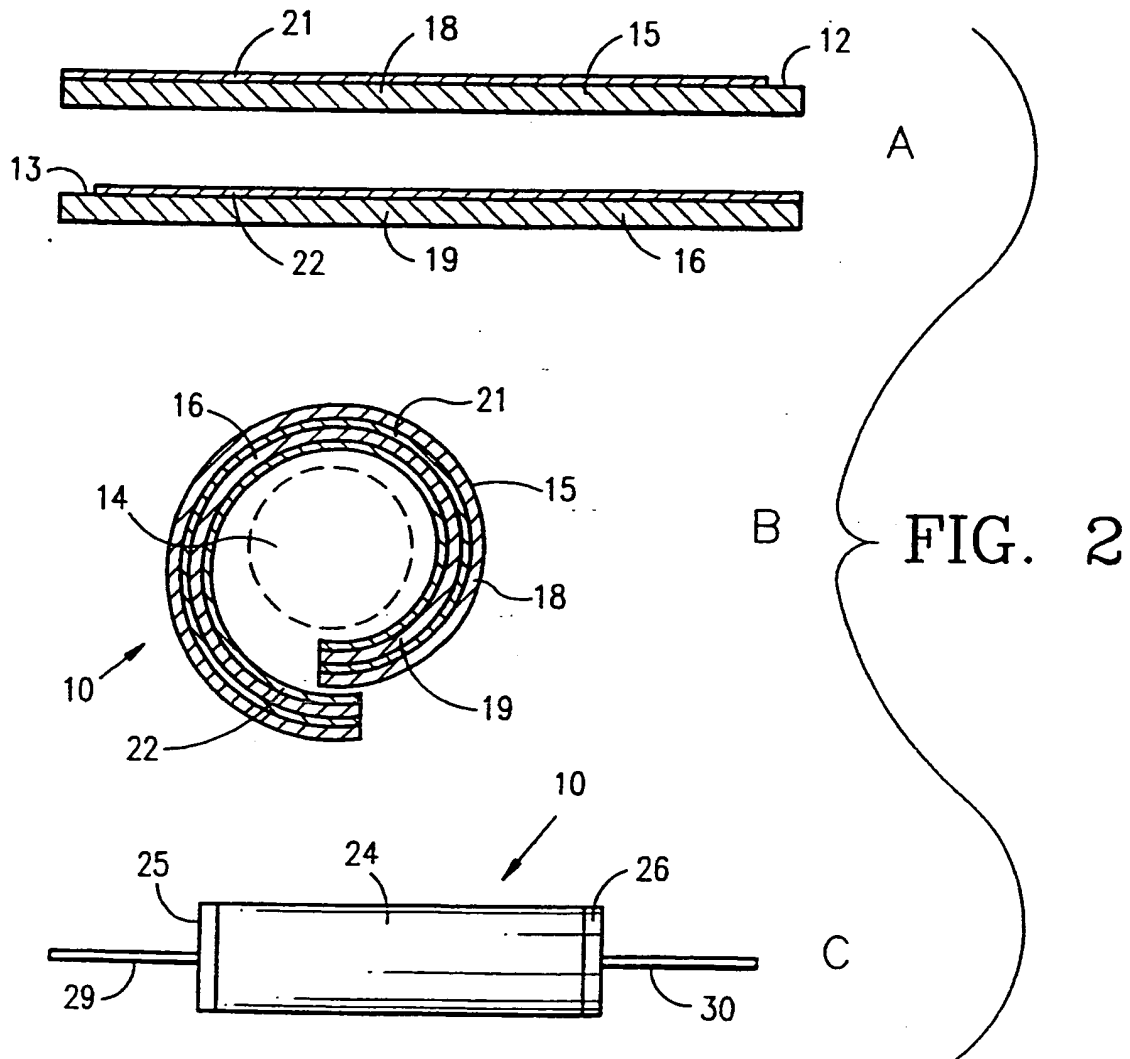


FIG. 1



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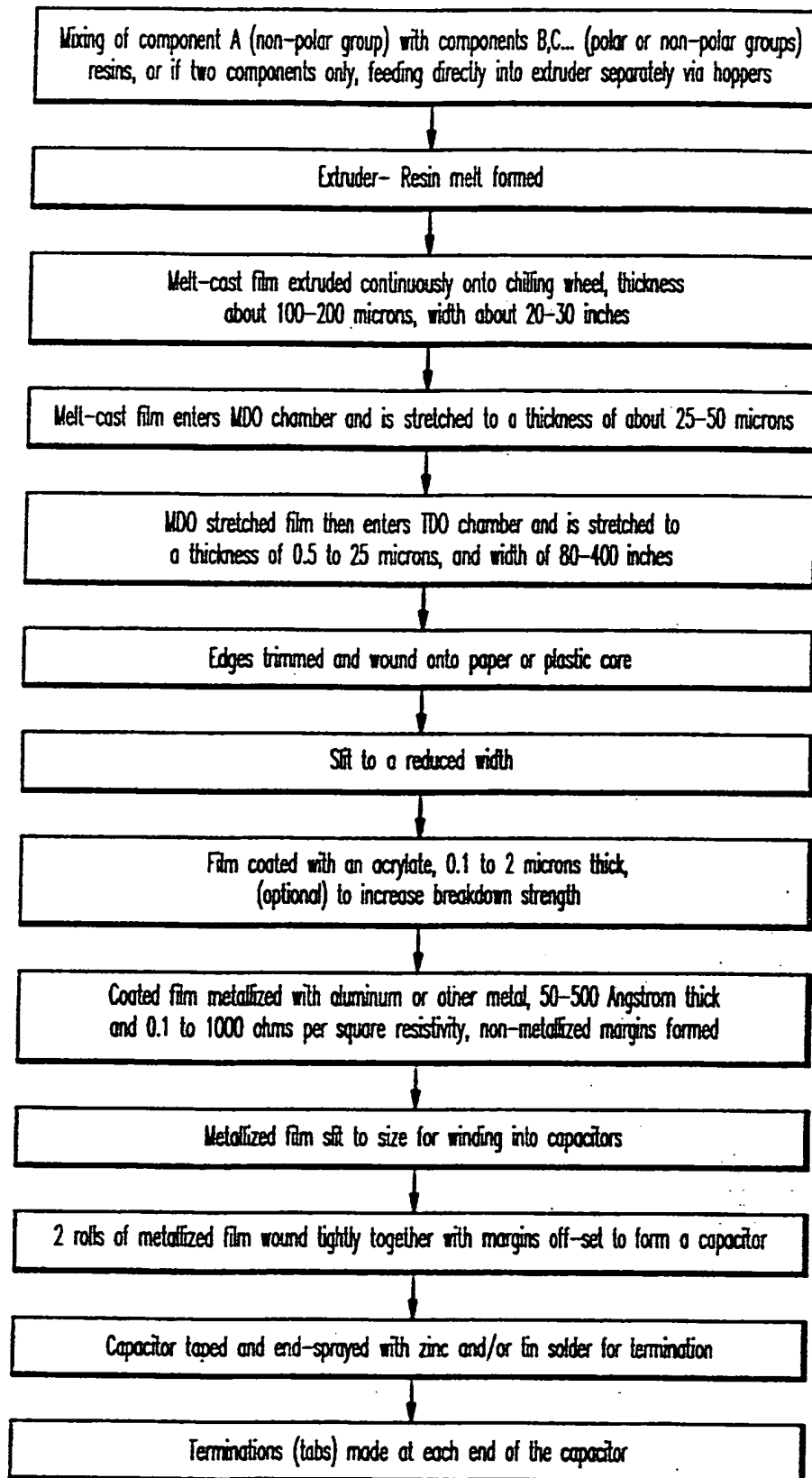


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/32276

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : Please See Extra Sheet.

US CL : 138/137, 138, 139; 428/34.1, 35.7.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 138/137, 138, 139; 428/34.1, 35.7.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST (dERWENT, USPAT). Search terms: polyvinylidene fluoride, polypropylene, oriented or stretched, vapor deposit, film, tube.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X — Y	US 5,700,564A (FREEDMAN) 23 December 1997, col. 2, lines 58 and 64-5; col. 3, lines 1-3; col. 10, lines 17 and 31.	1,3,6,11. — 2-4, 7, 10, 13, 15-16, 18-22, 25
X — Y	US 5,514,427A (ELLISON et al) 07 May 1996, col. 2, line 30, col. 3, lines 54-55; col. 4, lines 1-3, 23, 31-38 and 56.	1-6, 8, 10-11, 14, 16, 23-24, 26-27. — 2-4, 7, 10, 13, 15-16, 18-22, 25.



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

15 FEBRUARY 2001

Date of mailing of the international search report

03 APR 2001

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/32276

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 5,554,426A (ROBER et al) 10 September 1996, col. 3, lines 23 ans 26+; col. 4, lines 30-35, 47, and 55-63; col. 6, line 63.	1-5, 8, 11, 23- 24,26-27. ----- 2-4, 7,10, 13,15,16, 18-22, 25.
X --- Y	JP 63025024A, 02 February 1988, English Abstract, first and last paragraphs.	1-5,8,11-12, 14- 15,17, 23-24,26- 27. ----- 2-4, 7,10, 13,15-16, 18-22,25.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/32276

A. CLASSIFICATION OF SUBJECT MATTER:
IPC (7):

B29D 7/01, 9/00; B32B 1/08, 27/30.